A Photoswitchable Rotaxane with a Folded Molecular Thread

Werner Abraham,*[a] Lutz Grubert,[a] Ulrich W. Grummt,[b] and Karin Buck[a]

Dedicated to Professor Fritz Vögtle on the occasion of his 65th birthday

Abstract: Novel [2]rotaxanes containing the tetracationic cyclophane cyclobis(paraquat-4,4-biphenylene) and a dumbbell-shaped molecular thread incorporating a photoactive diarylcycloheptatriene station as well as a photoinactive anisol station have been synthesized with yields of nearly 50% by the alkylative endcapping method. The rotaxane was transformed into the related rotaxane incorporating a diaryl tropylium unit by electrochemical oxidation. The precursor of the cycloheptatrienyl rotaxane, the related pseudorotaxane, and the rotaxanes incorporating the diarylcycloheptatriene and the corresponding tropylium unit were characterized by ^{1}HNMR spectroscopy and UV/Vis spectroscopy. According to the NMR spectra, both the cycloheptatriene and the tropylium rotaxane possess a folded conformation enabling the tetracationic cyclophane to interact with two stations. The diarylcycloheptatriene station is incorporated inside the cavity of the cyclophane and the anisol station resides alongside the bipyridinium unit of the cyclophane. In contrast, the anisol station is inside the cyclophane in the tropylium rotaxane. The exchange between both conformations can be achieved by introducing the methoxy leaving group into the cycloheptatriene ring; the tropylium rotaxane is generated by photoheterolysis of this methoxy-substituted rotaxane, which reacts thermally back to the cycloheptatriene rotaxane, thus closing the switching cycle. These induced conformational changes achieve a so-called molecular machine.

Keywords: carbocations · cycloheptatrienes · photochemistry · rotaxanes · supramolecular chemistry

Introduction

The synthesis of mechanically linked supramolecules, such as catenanes and rotaxanes, has been developed as a standard method within the field of supramolecular chemistry;[1–4] today, research is focused on the function of supramolecules. Nature provides chemists with good examples of supramolecules, such as catalysts,[5] and molecular rotors[6] and machines,[7] and catenanes and rotaxanes have been successfully tested as components of molecular electronics.[8] The functionality is often based on a part within the supramolecule that is able to react to an outer stimulus such as chemical, light, or electrochemical energy;[7] the system response includes the change of the so-called co-conformation.[9]

Any stimulus usually causes a shuttling process of a ring component between two different subunits of a rather long chain, known as the molecular thread. These stations are characterized by different noncovalent interactions with the ring component; the outer stimulus alters the strength of this interaction.[10]

We have recently reported on the synthesis of rotaxanes with diarylcycloheptatrienes as stations within the molecular thread[11] and a tetracationic ring often used by Stoddart et al.[3] Charge-transfer interactions occur between the aryl cycloheptatriene electron donor and the bipyridinium electron acceptor of the ring component. Aryl cycloheptatrienes are interesting subunits of the molecular thread, because these seven-membered rings can be photochemically converted into the related tropylium ions.[12] The positive charge of the tropylium station should repulse the tetracationic ring resulting in a drastic change of the co-conformation of the rotaxane.

We report in this paper on the synthesis of rotaxanes with a photoactive diarylcycloheptatriene station and a second photoinactive anisole station; we also discuss the electrochemical and photochemical transformation into the corresponding tropylium rotaxane.

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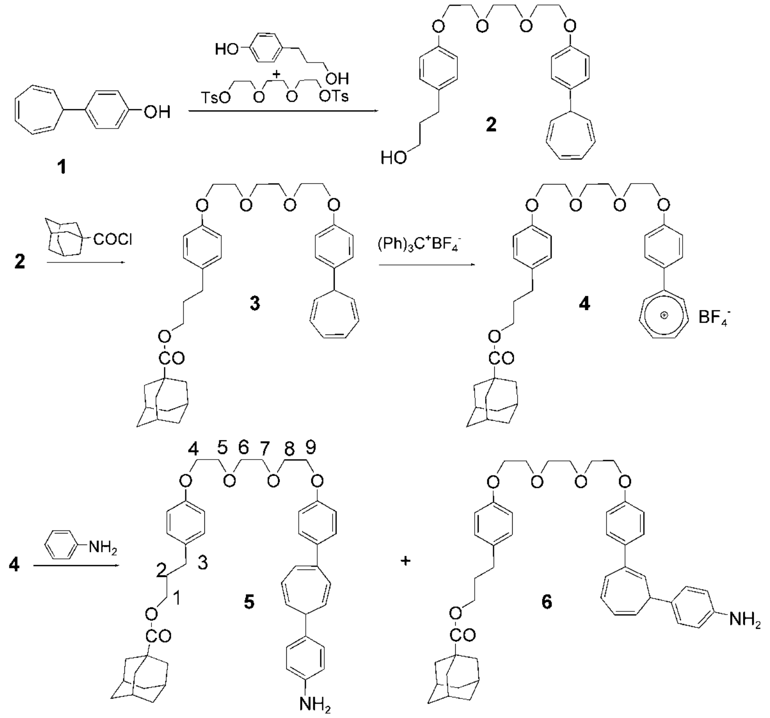
Results and Discussion

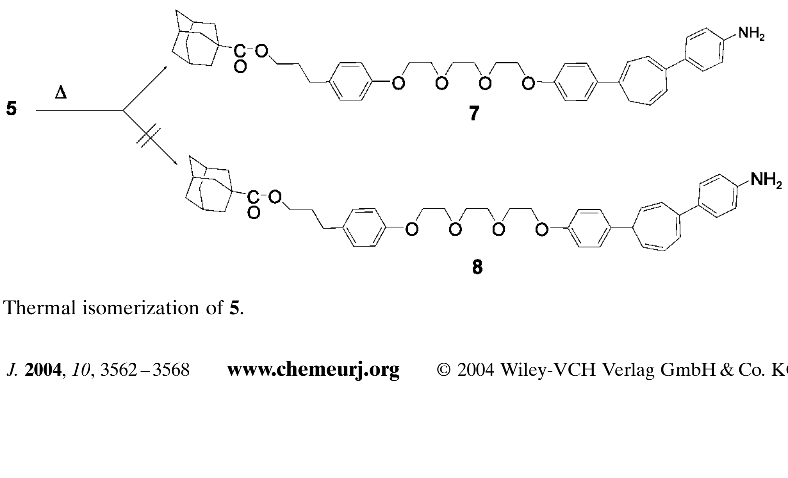
Syntheses: 7-(4-Hydroxyphenyl)-1,3,5-cycloheptatriene (**1**) is the building unit that allows the incorporation of the aryl cycloheptatriene (CHT) subunit into the molecular thread. The connection between the two different stations (CHT and anisole) was achieved directly to produce compound **2** with a 50% yield. The molecular thread was accomplished by the reaction of the tropylium salt **4** with aniline yielding the two isomeric compounds **5** and **6** in a ratio of approximately 2:1 (see Scheme 1); these can be separated by column chromatography. Only isomer **5** was used to synthesize rotaxanes. A second type of rotaxane, not considered here, is available by using isomer **6**.



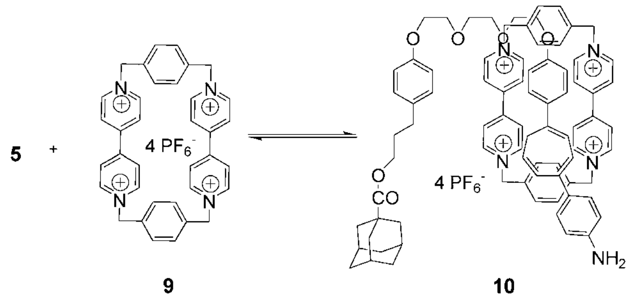
Scheme 1. Synthesis of the molecular thread **5**.

The molecular thread **5** was transformed into the isomeric compound **7** by a thermal hydrogen shift reaction; the alternative isomer **8** was not observed (Scheme 2).

The pseudorotaxane **10** is formed by mixing **5** with the tetracationic ring **9** in acetonitrile solution (see Scheme 3).



Scheme 2. Thermal isomerization of **5**.



Scheme 3. Formation of the pseudorotaxane **10**.

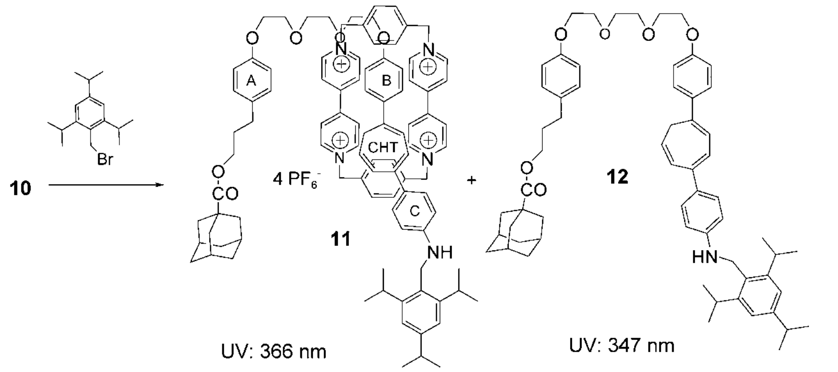
Besides the typical shifts of the proton signals, which will be discussed below, the pseudorotaxane can be detected by its weak charge-transfer absorption at 580 nm.

The amino group of **5** was alkylated giving the rotaxane **11** with a good yield of 50%. The second half of **5** was also alkylated; however, the product obtained was the uncomplexed free molecular thread **12** (Scheme 4).

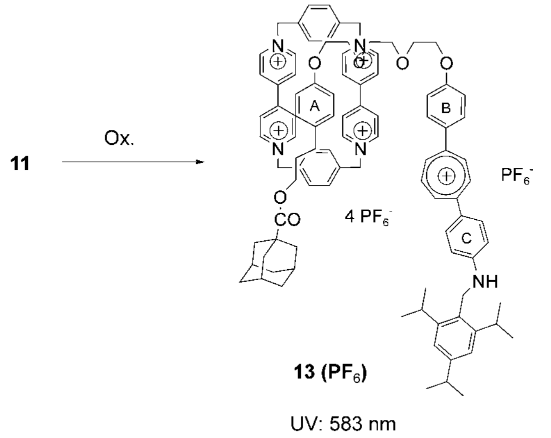
Electrochemical oxidation of rotaxane **11** yields rotaxane **13** on an almost quantitative basis (Scheme 5).

In the same way, the molecular thread **12** can be transformed to the tropylium salt **14**; this is needed in order to determine the chemical-induced shift (CIS) values by comparing **13** and **14**.

Co-conformation: There are two subunits (stations) in the molecular threads **5** and **12** that are able to bind the electron acceptor **9** by charge-transfer and electrostatic interactions; these are the aromatic ring A and the cycloheptatriene station, involving the two aromatic rings B and C, and the seven-membered ring (CHT) itself (see Scheme 4). However, the diaryl cycloheptatriene station has an oxidation potential of 0.5 V and the anisole station a potential of 1.5 V;[13] therefore, it can be expected that the tetracationic ring will reside exclusively on the diaryl cycloheptatriene station. ^{1}HNMR spectroscopy is the best method to explore the position of the ring **9** within the pseudorotaxane **10** and the rotaxanes **11** and **13**; the differences of the proton signals of the uncomplexed and complexed



Scheme 4. Synthesis of the rotaxane **11**.



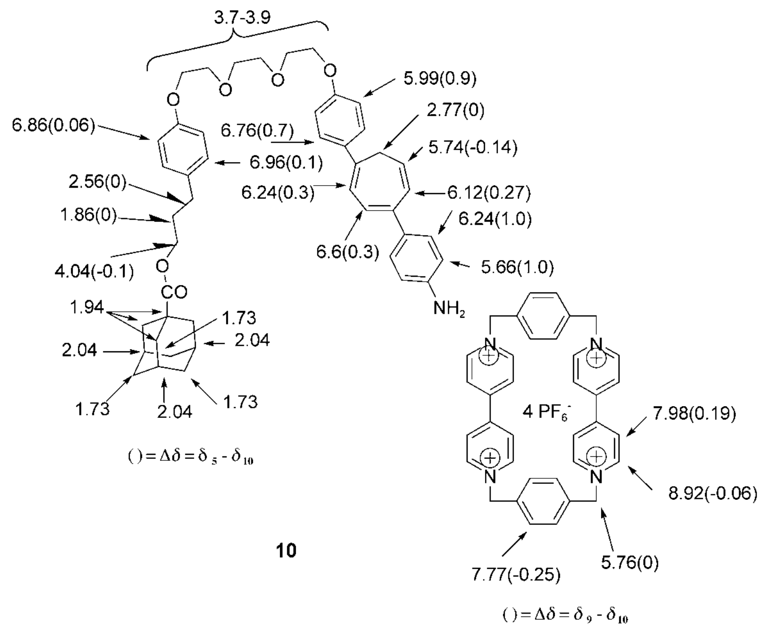
Scheme 5. Electrochemical oxidation of **11**.

molecular threads within the pseudorotaxane and the rotaxanes indicates the strength of the interaction between the stations and the ring by the chemical-induced shift ($\Delta\delta$, CIS values). The assignment of the proton signals to the different aromatic rings of the two stations is possible with the help of NOE effects (ROESY spectra).

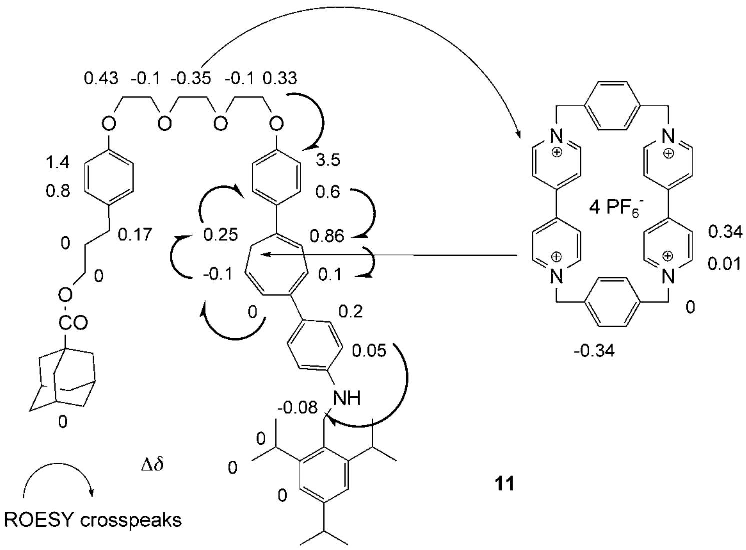
The results obtained with the pseudorotaxane **10** are summarized in Scheme 6. Only one set of signals can be observed for all protons, indicating a fast exchange between the pseudorotaxane and its free components. The negative CIS values (downfield shift) observed for the protons of the aromatics of the benzylic spacers within **9** and the positive CIS values (upfield shift) of the β-protons of the pyridinium units of **9** are typical of pseudorotaxanes.[3] It is worthwhile noting that apart from the bridging aromatic benzyl signals, all signals of **9** are rather broad in the 300 MHz NMR spectrum; accordingly, there must be a slow dynamic process relative to the 300 MHz timescale. Our interpretation of this finding is that there is restricted internal rotation of the bipyridinium rings of **9**.

The signals of the two aromatics of the cycloheptatriene station are also broadened. Considering the CIS values of the protons of the two stations, the ring resides on this station as expected. The strongest electron donor, aniline, interacts most strongly with the ring. The protons of the seven-membered ring (CHT) are modestly shifted, and the resonances of the protons of the second station are only marginally influenced. It is worthwhile noting that the absorption wavelength of the molecular thread is not altered under the influence of the complexation.

The findings with the rotaxane **11** are rather different (see Scheme 7). The strongest interaction is observed for ring B, whereas the proton resonances of C are only modestly shifted. According to the CIS values, the ring **9** mainly resides on B and the adjacent part of CHT. Surprisingly, a rather strong interaction of the station A is deduced from the CIS values. The proton resonances of both A and B are only visible at increased temperatures (see Supporting Information), because these signals merge with the base line between $\delta=$ 6 and 4 ppm at room temperature. In addition, the assignment of the proton signals to A and B was in this case only



Scheme 6. Proton resonances (in ppm) of the components of the pseudorotaxane and CIS values (in parenthesis).



Scheme 7. Proton CIS values ($\delta_{\text{free component}}-\delta_{\text{rotaxane}}$) of the components of **11**.

possible with the help of ROESY spectra at increased temperature. The temperature influence is attributable to the hindered rotation of the aromatic rings that are located in the vicinity of the tetracationic ring **9**. Upon warming up the solution of **11** and **9** in CD_3CN, a sharpening of the resonances of the bipyridinium protons of **9** is observed, indicating that the internal rotation of these subunits is restricted at room temperature.

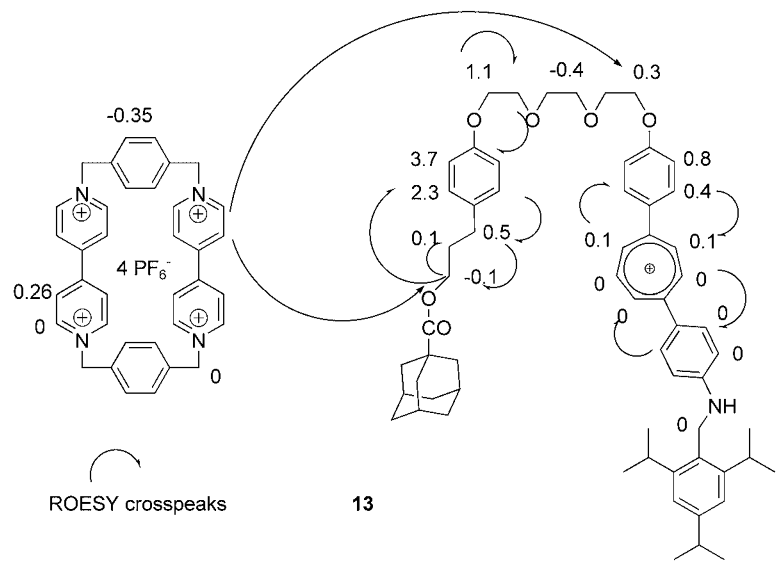
The surprising finding of the interaction of **9** with both A and B is most likely to relate to a folding of the glycol chain between the two stations thus bringing the two stations within the vicinity of the tetracationic ring. However, whereas station B is situated within the cavity of ring **9**, station A interacts with **9** from the outer sphere. The methylene protons adjacent to the phenol units resonate with a significant upfield shift, implying that on a time-averaged basis, these protons are oriented directly above and below the bipyridinium units of **9**. In contrast, the methylene proton resonances of the central portion of the chain experience downfield shifts by virtue of their lying in the plane of the bipyridinium rings. NOE effects between the pyridinium protons of **9** and the central methylene protons of the glycol chain, seen in the ROESY spectra recorded for rotaxane **11** in CD_3CN and in $[D_6]$acetone, reveal that these parts of the ring and the molecular thread are situated close together.

Due to the folded conformation, there are two different bipyridinium units in the cyclophane **9**, one interacts both with the cycloheptatriene station and station A, the other only interacts with the cycloheptatriene station. This results in the additional splitting of the signals of the β-protons of the bipyridinium units and of the benzylic protons of **9** (for the spectrum see Supporting Information).

The residence of the cyclophane **9** around the cycloheptatriene station leads to a bathochromic shift of the longest wavelength absorption of the diaryl cycloheptatriene chromophore by 19 nm compared with the uncomplexed molecular thread. We explain this effect by the very high polarity induced by the tetracationic ring around the chromophore. It is worthwhile noting that the same co-conformation of the rotaxane **11** is formed in aprotic solvents, such as CD_3CN, and protic solvents, such as the mixture CD_3OD/CD_3CN (5:1). The NMR spectra are identical in these solvents.

Due to the repulsion of the positive charges of the tropylium ion and the tetracationic ring, the latter should reside on the anisol station (A) in the tropylium rotaxane **13**. Indeed, the highest CIS values are found for this station (see Scheme 8); in addition, the assignment of the proton resonances is possible in this case with the help of ROESY spectra.

However, despite the charged tropylium ring, a significant interaction between ring B of the tropylium station and **9** is deduced from the CIS values determined for this subunit. Therefore, the folded conformation must also be assumed for the rotaxane **13**, enabling the interaction with ring A inside the cyclophane **9** and the interaction with ring B and one bipyridinium unit of **9**. Accordingly, and in keeping with the findings with rotaxane **11**, contacts between **9** and the central methylene protons of the glycol chain are observed in the ROESY spectra of **13**. In contrast to **11**, station A is in the inner of the cyclophane and ring B of the tropylium station interacts with **9** from one side only (see Scheme 5). Accordingly, the signals of both the α- and β-protons of the cyclophane are much broadened, and the resonance of the benzylic methylene protons of **9** appears as four signals.

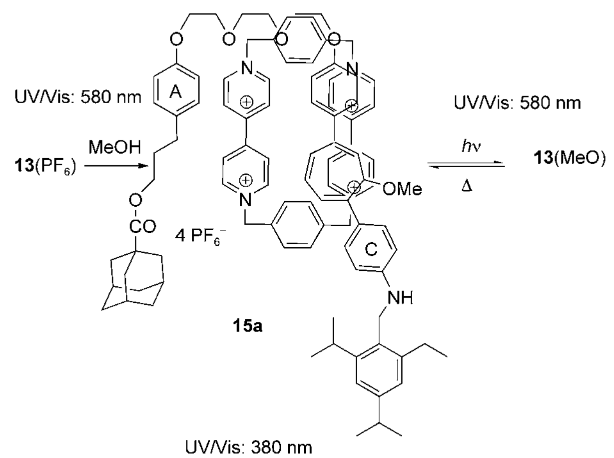


Scheme 8. Proton CIS values ($\delta_{\text{free component}} - \delta_{\text{rotaxane}}$) of the components of **13**.

As result, the positive charge of the tropylium ring does not hinder the interaction of the positively charged cyclophane with the adjacent aryl group B. Only the tropylium ring itself together with the adjacent ring C is uninfluenced by **9**.

Switching process: We have recently found that the alkoxy substituent is a suitable leaving group with which to photochemically generate aryl tropylium ions from their related cycloheptatrienes.[12]

This method can be used to transform rotaxanes of type **11** to the tropylium rotaxane **13**. By simply dissolving the rotaxane **13** in methanol in the presence of $NaHCO_3$, methoxy derivatives of the rotaxane **11** are formed by nucleophilic attack on the tropylium ring, accompanied by the slow decrease of the tropylium salt absorption band at 680 nm and the appearance of the UV-absorption band at 380 nm. In principle, all the carbon atoms of the seven-membered ring may be attacked by the methoxy group; however, those positions that allow a conjugative interaction of the two aryl substituents across the cycloheptatriene ring are thermodynamically preferred. In fact, there are at least three isomeric rotaxane derivatives. According to ^{1}HNMR and ROESY spectra of the mixture of the methoxy derivatives of **11**, the preferred formation of compound **15a** is revealed (see Scheme 9). The longest wavelength of **15** corresponds to a



Scheme 9. The switching process.

coupling of the two aryl substituents across the π-system of the seven-membered ring.[14] Both the CIS values of the proton resonances of the cycloheptatriene ring and ring C, as well as the lack of the proton signals of A and B at room temperature that appear at higher temperatures, indicate the similarity between the rotaxanes **11** and **15**. Neither the arrangement of the π-bonds within the seven-membered ring, the presence of the methoxy group, nor changing the solvent acetonitrile to methanol affects the interaction of the cyclophane **9** with the cycloheptatriene station.

Apart from the NMR spectra, two findings reveal that **9** resides on the CHT station: 1) the UV-absorption band of the methoxycycloheptatriene station of **15** is bathochromically shifted by 20 nm relative to the related absorption band of the uncomplexed molecular thread, and 2) even in methanol a weak charge-transfer absorption of around 600 nm is recorded.

By excitation of the weakly yellowish solution of **15** in methanol under the conditions of a conventional flash photolysis at 360 nm, a transient absorption around 590 nm is observed. The spectral properties of this transient absorption correspond to the tropylium rotaxane **13** with a methoxide counterion (see Scheme 9 and Supporting Information). We were unable to generate the tropylium rotaxane from **15** by excitation of the charge-transfer transition (600 nm).

The lifetime of the ionic state is 15 s, this is significantly higher than that of the model compound 3-(4-dimethylamino)-7-methoxycycloheptatriene.[12] The efficiency of the photoheterolysis of the rotaxane is reduced by one order of magnitude relative to that of the uncomplexed molecular tropylium thread; however, the number of possible heterolysis cycles without fading is much higher than that of the comparable compound. Both effects are due to the charge-transfer interaction. The low-energy charge-transfer level causes additional nonradiative deactivation of the excited state of the rotaxane **15**. Surprisingly, the competing photoreactions, such as the sigmatropic hydrogen shift and electrocyclization of diaryl cycloheptatrienes,[14] are quenched much more than the photoheterolysis reaction, resulting in a much higher photostability of the rotaxane **15**. Preliminary studies have shown that after ten cycles of photoheterolysis and the following thermal back reaction, no fading of the system could be detected.

Conclusion

For the first time the principle of photoheterolysis has been successfully used to switch the position of the tetracationic ring **9** within a rotaxane. By creating the positive charge in the molecular thread, a drastic change of the co-conformation of the rotaxane is induced that is reversible by a thermal reaction. Thus, this is in principle, a simple approach to a so called molecular machine that is driven by light and thermal energy.[7]

Experimental Section

General methods: MeCN was distilled over CaH_2. Silica gel 60 (0.040–0.063 mm) (Fluka) was used for column chromatography (CC). Melting points (m.p.) were determined with a Boetius heating microscope. NMR spectra were recorded on a Bruker DPX 300 (300 MHz), Bruker Advance 400 (400 MHz) or a Bruker AMX 600 (600 MHz) spectrometers. UV/Vis spectra were recorded with a Shimadzu UV 2101 PC spectrometer. The flash photolysis equipment was described in reference [15]. Rapid scan (1 to 50 $V s^{-1}$) cyclic voltammetry was performed using a PG 285 IEV potentiostat (HEKA Elektronik).

Synthesis of 7: A solution of compound **1** (3.9 g, 21.6 mmol), 3-(4-hydroxyphenyl)propanol (3.28 g, 21.6 mmol), und NaOEt (4.4 g, 64.8 mmol) in MeCN (250 mL) was stirred for 30 min at room temperature. After that time the solution was heated under reflux and triethylenglykolbistosylate (9.8 g, 21.8 mmol) in MeCN (50 mL) was added dropwise into the solution. Refluxing was continued for 6 h. The solvent was removed under reduced pressure and the remaining mixture was worked up by CC (silica gel, cyclohexane/acetone 3:1) thus separating **2** from the symmetric substitution products; oil, 4.45 g (50%).

Without further purification **2** (3.76 g, 8.34 mmol) was treated with adamantane-1-carbonyl chloride (1.82 g, 9.17 mmol) in pyridine (9 mL) for 4 h at 75 °C. The reaction mixture was poured to dilute HCl (15 mL). The aqueous solution was extracted several times using dichloromethane as solvent, and the organic phases were washed with a saturated aqueous solution of NaCl, dried (Na_2SO_4), and evaporated. The ester **3** (4.64 g, 91%) was oxidized without further purification by using trityl tetrafluoroborate (2.51 g, 7.57 mmol) in dichloromethane affording **4**, which was purified by treating the solid with a mixture of ethyl acetate (10 mL) und methyl-*tert*-butylester (MTBE) (40 mL). The tropylium salt **4** (3.7 g, 5.3 mmol) dissolved in dichloromethane (30 mL) was added to aniline (1.79 g, 19.2 mmol). After stirring for 5 h at room temperature the solution was washed with an aqueous solution of $NaHCO_3$, the organic phase was dried (Na_2SO_4), and the solvent was removed under reduced pressure. The isomer **5** was separated from **6** by CC (silica gel, toluene/ethyl acetate 8:1, oil, 940 mg (25%). ^{1}H NMR (300 MHz, CD_3CN, TMS): δ = 1.71, 1.85, 1.93 (br m, 17 H; adamantane, 1-H), 2.60 (t, J(H,H) = 8 Hz, 2 H; 3-H), 2.69 (t, J(H,H) = 6 Hz, 1 H; CHT, 7-H), 3.64 (s, 4 H; 6-H, 7-H), 3.77 (m, 4 H; 5-H, 8-H), 3.96 (t, J(H,H) = 6 Hz, 2 H; 1-H), 4.1, 4.05 (m, 4 H; 4-H, 9-H), 5.43 (m, 1 H; CHT, 6-H), 5.52 (m, 1 H; CHT, 1-H), 6.29 (m, 1 H; CHT, 5-H), 6.34 (d, J(H,H) = 10 Hz, 1 H; CHT, 2-H), 6.66 (d, J(H,H) = 8 Hz, 2 H; ring C), 6.83 (d, J(H,H) = 9 Hz, 2 H; A), 6.94 (d, J(H,H) = 9 Hz; ring B), 7.04 (d, J(H,H) = 6 Hz, 1 H; CHT, 4-H), 7.09 (d, J(H,H) = 9 Hz, 2 H; ring A), 7.11 (d, J(H,H) = 8 Hz, 2 H; ring C), 7.45 ppm (d, J(H,H) = 9 Hz, 2 H; ring B).

The solution of **5** (1 g, 1.4 mmol) in toluene (150 mL) was heated under reflux for 11 h. After removing the solvent the isomer **7** resulted as an oil, which was used for the synthesis of the rotaxane without further purification. ^{1}H NMR (300 MHz, CD_3CN, TMS): δ = 1.71, 1.85, 1.93 (br m, 17 H; adamantane), 2.60 (t, J(H,H) = 8 Hz, 2 H; 3-H), 2.76 (d, J(H,H) = 8 Hz, 2 H; CHT, 7-H), 3.64 (s, 4 H; 6-H, 7-H), 3.76 (m, 4 H; 5-H, 8-H), 3.96 (t, J(H,H) = 6 Hz, 2 H; 1-H), 4.04, 4.1 (m, 4 H; 4-H, 9-H), 5.6 (m, 1 H; CHT, 6-H), 6.39 (d, J(H,H) = 10 Hz,1 H; CHT, 5-H), 6.34 (d, J(H,H) = 10 Hz, 1 H; CHT, 2-H), 6,65 (d, J(H,H) = 9 Hz, 2 H; ring C), 6.80 (d, J(H,H) = 9 Hz, 2 H; ring A), 6.89 (d, J(H,H) = 9 Hz; ring B), 6.97 (d, J(H,H) = 6 Hz, 1 H; CHT, 3-H), 7.07 (d, J(H,H) = 9 Hz, 2 H; ring A), 7.27 (d, J(H,H) = 9 Hz, 2 H; ring C), 7.44 ppm (d, J(H,H) = 9 Hz, 2 H; ring B).

Pseudorotaxane 10: Compound **7** (0.007 g, 0.0098 mmol) together with **9** (0.011 g, 0.010 mmol) was dissolved in CD_3CN (1.5 mL) in order to measure ^{1}HNMR spectra (see Supporting material).

Rotaxane 11: Compound **7** (0.39 g, 0.55 mmol) dissolved in dichloromethane (1.5 mL) was added to a solution of **9** (0.73 g, 0.66 mmol) in acetonitrile (6 mL). Dichloromethane was then removed under reduced pressure. 2,4,6-Tris(isopropyl)benzyl bromide (0.163 g, 0.55 mmol) together with 2,6-di-*tert*-butyl-4-methylpyridine (0.113 g, 0.55 mmol) dissolved in acetonitrile (2 mL) was added to the green solution of the pseudorotaxane. The reaction solution was stirred under an argon atmosphere for 48 h at room temperature, the solution was evaporated, and the residue was extracted with MTBE (75 mL). From the filtrate compound **12** formed as oil (0.23 g. 45%). ^{1}H NMR (300 MHz, CD_3CN, 303 K, TMS): δ = 1.23 (d, J(H,H) = 7 Hz, 18 H; *i*Pr), 1.71, 1.85, 1.95 (br m, 17 H; adamantane, 2-H), 2.61 (t, J(H,H) = 8 Hz, 2 H; 3-H), 2.79 (d, J(H,H) = 7 Hz, 2 H; CHT, 7-H), 2.90 (sep, J(H,H) = 7 Hz, 1 H; *i*Pr), 3.21 (sep, J(H,H) = 7 Hz, 2 H; *i*Pr), 3.65 (m, 4 H; 6-H, 7-H), 3.80 (m, 4 H; 5-H, 8-H), 3.97 (t, J(H,H) = 6 Hz, 2 H; 1-H), 4.06 (m, 2 H; 8-H), 4.10 (m, 2 H; 5-H), 4.23 (s, 2 H; N-benzyl), 5.61 (m, 1 H; CHT, 6-H), 6.43 (d, J(H,H) = 9 Hz,1 H; CHT, 5-H), 6.54 (d, J(H,H) = 9 Hz,1 H; CHT, 2-H), 6.73 (d, J(H,H) = 9 Hz, 2 H; ring C), 6.83 (d, J(H,H) = 9 Hz, 2 H; ring A), 6.91 (d, J(H,H) = 9 Hz, 2 H; ring B), 6.99 (m, 1 H; 3-CHT) 7.08 (d, J(H,H) = 9 Hz, 2 H; ring A), 7,10 (s, 2 H; *i*Pr-Ph), 7.38 (d, J(H,H) = 9 Hz, 2 H; ring C), 7.50 ppm (d, J(H,H) = 9 Hz, 2 H; ring B).

The solid insoluble in MTBE was purified by column chromatography on neutral Al_2O_3 (Fluka) by using a solvent mixture of acetonitrile (400 mL), ethyl acetate (200 mL), and cyclohexane (100 mL) containing ammonium hexafluorophosphate (7 g). The green fraction was concentrated under reduced pressure and the resulting solid was washed with water (350 mL) and MTBE (75 mL). Rotaxane **11** was formed as a yellowish-green solid (mp 199–201 °C, 0.53 g, 47%). ^{1}H NMR (600 MHz, CD_3CN, 333 K, TMS): δ = 1.27 (d, J(H,H) = 7 Hz, 6 H; *i*Pr), 1.29 (d, J(H,H) = 7 Hz, 12 H; *i*Pr), 1.71, 1.91, 2.03 (br m, 17 H; adamantane, 2-H), 2.43 (t, J(H,H) = 8 Hz, 2 H; 3-H), 2.54 (d, J(H,H) = 7 Hz, 2 H; CHT, 7-H), 2.92 (sep, J(H,H) = 7 Hz, 1 H; *i*Pr), 3.27 (sep, J(H,H) = 7 Hz, 2 H; *i*Pr), 3.67 (m, 2 H; 4-H), 3.73 (m, 2 H; 9-H), 3.9 (m, 8 H; 5-H, 6-H, 7-H, 8-H), 3.99 (t, J(H,H) = 6 Hz, 2 H; 1-H), 4.31 (br s, 2 H; N-Benzyl), 4.60 (br d, 2 H; ring B), 5.4 (br d, 2 H; ring A), 5.52 (br d, 2 H; ring B), 5.68 (d, J(H,H) = 7 Hz, 1 H; CHT, 2-H), 5.79, 5.76, 5.75, 5.74, 5.73 (m, 9 H; cyclophane, CHT, H-6) 6.3 (br d, 2 H; ring A), 6.43 (d, J(H,H) = 9 Hz,1 H; CHT, 5-H), 6,68 (d, J(H,H) = 8 Hz, 2 H; ring C), 6.90 (d, J(H,H) = 7 Hz, 1 H; CHT, 3-H), 7.14 (s, 2 H; *i*Pr-Ph), 7.36 (d, J(H,H) = 8 Hz, 2 H; ring C), 7.82 (d, J(H,H) = 7 Hz, 8 H; cyclophane), 7.86 (s, 8 H; cyclophane), 8.87 ppm (d, J(H,H) = 7 Hz, 8 H; cyclophane); MS (ESI): m/z: 864.8815 $[M-2PF_6]^+$ (calcd for $[C_{97}H_{109}F_{12}N_5O_6P_2]$: 864.8831), 526.2268 $[M-3PF_6]^+$ (calcd for $[C_{97}H_{109}F_6N_5O_6P]$: 528.2673), 359.9592 $[M-4PF_6]^+$ (calcd for $[C_{97}H_{109}N_5O_6]$: 359.9594).

Rotaxane 13: A solution of rotaxane **11** (0.10 g, 0.05 mmol) in MeCN containing Et_4NPF_6 (0.1 M, 50 mL) was oxidized by a controlled potential electrolysis (E_A = 0.9–1.2 V [SCE], HEKA PG285) at a Pt electrode in the anode region of an H cell until a charge output of 2 F mol^{-1} was consumed. After evaporating and washing with water, the remaining blue solid was purified by column chromatography (silica gel, acetonitrile (400 mL), ethyl acetate (200 mL), cyclohexane (100 mL) containing ammonium hexafluorophosphate (7 g)). Rotaxane **13** (0.10 g, 94%) was obtained as a blue solid. M.p. 208 °C (decomp); ^{1}H NMR (600 MHz, CD_3CN, TMS): δ = 1.25 (d, J(H,H) = 7 Hz, 18 H; *i*Pr), 1.7 (m, 2 H; 2-H), 1.8, 2.0, 2.1 (br m, 17 H; adamantane, 3-H), 2.43 (t, J(H,H) = 8 Hz, 2 H; 3-H), 2.91 (sep, J(H,H) = 7 Hz, 1 H; *i*Pr), 2.99 (br m, 2 H; 4-H), 3.1 (br s, 2 H; ring A), 3.16 (sep, J(H,H) = 7 Hz, 2 H; *i*Pr), 3.95 (br m, 2 H; 9-H), 4.0 (br m, 6 H; 5-H, 6-H, 7-H, 8-H), 4.05 (t, J(H,H) = 7 Hz, 2 H; 1-H), 4.48 (d, J(H,H) = 4 Hz, 2 H; N-benzyl), 4.80 (br d, 2 H; ring A), 5.70, 5.72, 5.75, 5.77 (m, 8 H; cyclophane), 5.99 (t, J(H,H) = 4 Hz, 1 H; NH), 6.31 (br, 2 H; ring B), 6.97 (d, J(H,H) = 9 Hz, 2 H; ring C), 7.14 (s, 2 H; aromatic), 7.4 (br d, 2 H; ring B), 7.82 (s, 8 H; cyclophane), 7.9 (br s, 8 H; cyclophane), 8.00 (d, J(H,H) = 9 Hz, 2 H; ring C), 8.27 (m, 1 H; tropylium, 7-H), 8.31 (t, J(H,H) = 10 Hz, 1 H; tropylium, 6-H), 8.42 (dd, J(H,H) = 12; 2 Hz, 1 H; tropylium, 2-H), 8.72 (br m, 1 H; tropylium, 5-H), 8.81 (dd, J(H,H) = 12; 2 Hz, 1 H; tropylium, 3-H), 8.89 ppm (d, J(H,H) = 7 Hz, 8 H; cyclophane); UV/Vis (MeCN): λ_{max} (ε) = 583 (50000), 387 (10800), 262.5 nm (66720 mol^{-1}dm^{3}cm^{-1}); elemental analysis calcd (%) for $C_{97}H_{108}F_{30}N_5O_6P_5$ (2163.6509): C 53.80, H 5.03, N 3.24; found: C 53.86, H 5.12, N 3.34.

Molecular thread 14: A soultion of compound **12** (0.14 g, 0.15 mmol) in MeCN containing Et_4NPF_6 (0.1 M, 50 mL) was oxidized by a controlled potential electrolysis (E_A = 0.9–1.2 V [SCE], HEKA PG285) at a Pt electrode in the anode region of a H cell until a charge output of 2 F mol^{-1} was consumed. After evaporating and washing with water, the remaining blue solid was purified by column chromatography (silica gel, acetonitrile (400 mL), ethyl acetate (200 mL), cyclohexane (100 mL) containing ammonium hexafluorophosphate (7 g)). Compound **14** (0.13 g, 79%) was obtained, as it was necessary to record its NMR spectrum in order to calculate the CIS values of **13**. M.p. 80 °C (decomp); ^{1}H NMR (600 MHz, CD_3CN, TMS): δ = 1.24 (d, J(H,H) = 7 Hz, 18 H; *i*Pr), 1.7 (m, 2 H; 2-H), 1.8, 2.0, 2.1 (br m, 15 H; adamantane), 2.58 (t, J(H,H) = 8 Hz, 2 H; 3-H), 2.91 (sep, J(H,H) = 7 Hz, 1 H; *i*Pr), 3.16 (sep, J(H,H) = 7 Hz, 2 H; *i*Pr), 3.66 (m, 4 H; 6-H, 7-H), 3.76 (m, 2 H; 5-H), 3.83 (m, 2 H; 8-H), 3.95 (t, J(H,H) = 7 Hz, 2 H; 1-H), 4.03 (m, 2 H; 4-H), 4.48 (d, J(H,H) = 4 Hz, 2 H; N-benzyl), 5.91 (t, J(H,H) = 4 Hz, 1 H; NH), 6.81 (d, J(H,H) = 9 Hz, 2 H; ring A), 6.95 (d, J(H,H) = 9 Hz, 2 H; ring C), 7.14 (s, 2 H; *i*Pr-Ph), 7.16 (d, J(H,H) = 9 Hz, 2 H; ring B), 7.79 (d, J(H,H) = 9 Hz, 2 H; ring B), 7.96 (d, J(H,H) = 9 Hz, 2 H; ring C), 8.28 (t, J(H,H) = 12; 1 H; tropylium, 6-H), 8.39 (dd, J(H,H) = 12; 2 Hz, 1 H; tropylium, 7-H), 8.56 (dd, J(H,H) = 12; 2 Hz, 1 H; tropylium, 2-H), 8.67 (dd, J(H,H) = 12; 2 Hz, 1 H; tropylium, 5-H), 8.78 ppm (dd, J(H,H) = 12; 2 Hz, tropylium 3-H); UV/Vis (acetonitrile): λ_{max} (ε) = 583 (50000), 387 (10800), 262.5 nm (66720 mol^{-1}dm^{3}cm^{-1}); MS (ESI): m/z: 918.5673 $[C_{61}H_{76}NO_6]^+$ (calcd: 918.5673).

Methoxy-substituted rotaxanes 15: The isomeric mixture of the methoxy derivatives **15** was obtained by addition of methanol (0.1 mL) to a solution of **13** (20 mg) in MeCN (2 mL) that contained $NaHCO_3$ (20 mg).

After stirring for 4 h the blue color disappeared. After filtration the solvent was removed under reduced pressure. In order to record the NMR spectra the solid was dissolved with CD_3CN (0.1 mL) and diluted with CD_3OD to 0.6 mL. The spectra [^{1}HNMR (see Supporting Information), H-H-COSY und ROESY] show the presence of the main isomer **15a**. MS (ESI): 1904.76 [M^+-PF_6], 879.89 [$M-2PF_6$]$^{2+}$, 538.27 [$M-3PF_6$]$^{3+}$, 367.46 [$M-4PF_6$]$^{4+}$.

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